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**ON THE DIELECTRIC CONSTANTS OF PURE SOLVENTS**

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BY

**HERMAN SCHLUNDT, M. S.**

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**A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY,  
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## ON THE DIELECTRIC CONSTANTS OF PURE SOLVENTS.

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### Introduction.

In 1893 Nernst,<sup>1</sup> from theoretical considerations based upon the theory of electrolytic dissociation, deduced his well known rule, that—other things being equal—the greater the dielectric constant of a medium the greater is its dissociating power. In the same year J. J. Thomson<sup>2</sup> also pointed out this relation, saying that if we accept the view that the forces between the atoms are electrical in their origin then the effect of surrounding the molecules of a substance by a medium possessing a very high dielectric constant like water, would be to practically dissociate them. According to Nernst, proportionality between the dielectric constant and dissociating power need not necessarily exist, but a close parallelism between the two doubtless prevails. He adds that other factors besides the dielectric constant doubtless exist, which probably influence the dissociating power of the solvent. The experimental facts, Nernst<sup>3</sup> says, show beyond a doubt that a marked parallelism exists between the dissociating power and the dielectric constant. Exceptions to the rule he explains by assuming the existence of specific influences, of which the association of the ions with the molecules of the solvent is probably of prime importance.

The existing experimental data at the time the above relation between the dielectric constant and dissociating power was pointed out accorded well with it, and subsequent investigations furnished numerous additional examples in support of it. But

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<sup>1</sup> *Göttinger Nachrichten* No. 12, (1893); *Zeit. phys. Chem.* 13, 531, (1894).

<sup>2</sup> *Phil. Mag.* 36, 320, (1893).

<sup>3</sup> *Theoretische Chemie* p. 365. (Dritte Auflage).

exceptions also appeared which point to a marked specific influence of the solvent. Some of these exceptions are noted and considered in another part of this paper.

The following table taken from Nernst's<sup>1</sup> Theoretical Chemistry illustrates the general parallelism between the dielectric constant and the dissociating power.

TABLE I.

Medium.	Dielectric Constant.	Electrolytic Dissociation.
Gas.....	1.0	Not perceptible at ordinary temperatures.
Benzene .....	2.3	Exceedingly low; but distinctly perceptible conductivity indicates traces of dissociation.
Ether .....	4.1	Perceptible conductivity of dissolved electrolytes.
Alcohol .....	25	Dissociation quite marked.
Formic acid .....	62	Marked dissociation of dissolved salts.
Water .....	80	Very marked dissociation.

Since the formulation of the Nernst-Thomson rule excellent new methods for determining dielectric constants have been devised by Thwing,<sup>2</sup> Nernst,<sup>3</sup> and Drude;<sup>4</sup> and these investigators have measured the dielectric constants of a number of substances. The pupils of Nernst, and of Drude, and others have elaborated, modified and perfected these methods, so that the determination of dielectric constants at ordinary temperatures is now a comparatively simple operation. During this period the electrical conductivity of non-aqueous solutions has also received considerable study, and the dissociating power of various solvents, which yield conducting solutions, has moreover been investigated by means of cryoscopic and boiling-point determinations. The selected examples given in the following table will serve to show that various other solvents besides water possess ionizing power in a very marked degree. Under V, in the third

<sup>1</sup> P. 365, third edition. (1900).

<sup>2</sup> Phys. Review, 2, 35. (1894). Also Zeit. phys. Chem. 14, 288. (1894).

<sup>3</sup> Zeit. phys. Chem. 14, 622. (1894).

<sup>4</sup> Zeit. phys. Chem. 23, 287. (1897).



column, the volume in liters is given in which one gram molecule of substance is dissolved; and the next column gives the corresponding molecular conductivity, while the fifth column gives the temperature at which the measurements were made.

TABLE II.

Solvent	Solute	V	$U_v$	t°C	Observer
Water.....	KI	2	99.7	18	Kohlrausch <sup>1)</sup>
		100	116.1		
		1000	120.3		
Methyl alcohol .....	LiCl	11.7	40.1	18	Völlmer <sup>2)</sup>
		117.4	57.5		
		1174.0	65.3		
Formic acid .....	KCl	32	40.7	25	Zanninovich-Tessarini <sup>3)</sup>
		1024	57.8		
Liquid ammonia .....	K Br	301.9	210.6	-38	Franklin and Kraus <sup>4)</sup>
		1354	272.9		
		65040	340.2		
Liquid sulphur dioxide..	$N(C_2H_5)_4 I$	16	43.1	0	Walden <sup>5)</sup>
		128	51.6		
		1024	54.8		
Acetone.....	KI	144.7	106.4	18	St. v. Lascynski <sup>6)</sup>
		1157.6	145.8		
Benzonitrile .....	Ag NO <sub>3</sub>	9.43	5.2	25	Lincoln <sup>7)</sup>
		151.96	16.4		
Acetonitrile .....	Ag NO <sub>3</sub>	8	54.5	25	Dutoit and Friderich <sup>8)</sup>
		128	118.3		
Pyridine .....	NH <sub>4</sub> I	79	16.7	25	St. v. Lascynski and St. v. Gorski <sup>9)</sup>
		1264.32	36.9		
Phosphorus oxy-chloride	$S(CH_3)_3 I$	204	26.4	25	Walden <sup>10)</sup>
		1224	38.2		
Arsenic trichloride .....	$S(CH_3)_3 I$	250	51.4	25	Walden <sup>10)</sup>
		1500	66.6		

<sup>1)</sup> Wied. Ann. 26, 161. (1885).<sup>2)</sup> Wied. Ann. 52, 323. (1894).<sup>3)</sup> Zeit. phys. Chem. 19, 251. (1899).<sup>4)</sup> Am. Chem. Jour. 23, p. 238. (1900).<sup>5)</sup> Ber. d. Deutsch. Chem. Gesel. 32, 2882. (1899).<sup>6)</sup> Zeit. Elektrochem. 2, 55. (1896).<sup>7)</sup> Jour. Phys. Chem. 3, 457. (1899).<sup>8)</sup> Bull. Soc. Chem. [3] 19, 327. (1898).<sup>9)</sup> Zeit. Elektrochem. 4, 290. (1897).<sup>10)</sup> Zeit. anorg. Chem. 25, 209. (1900).

The dielectric constants of the last four solvents given in the table have, to my knowledge, not been determined before. That these solvents possess marked dissociating power the results given in the table clearly show. Hence by the Nernst-Thomson rule they should have high values for their dielectric constants. The dielectric constant of benzonitrile was measured by Drude,<sup>1</sup> and found to be 26.0 at 21° C. Drude also measured the dielectric constant of benzyl cyanide, but his extensive investigation does not include any of the nitriles of the aliphatic series. The dielectric constant of liquid ammonia was measured by Goodwin and Thompson<sup>2</sup> who found the value 22.0 at -34° C., and by Coolidge,<sup>3</sup> who gives the value 16.2 at 14° C. The substituted ammonias, Prof. Kahlenberg<sup>4</sup> finds, also yield good conducting solutions. In view of the great dissociating power of the nitriles and the substituted ammonias it seemed of special interest to determine the dielectric constants of these compounds, and at Prof. Kahlenberg's suggestion this work was undertaken. The investigation also embraces a number of other organic compounds containing nitrogen, and includes most of the inorganic solvents in which Walden<sup>5</sup> made electrical conductivity measurements.

During the progress of his researches on non-aqueous solutions, Prof. Kahlenberg collected a choice lot of preparations which he kindly placed at my disposal. This greatly facilitated the experimental part of my work, and I desire to express to him my thanks for this favor.

#### Method and Apparatus.

In measuring the dielectric constants the method devised and elaborated by Drude<sup>6</sup> was used. It is unnecessary for me to give a complete description of this method and of the details of

<sup>1</sup> Zeit. phys. Chem. 23, 309. (1897).

<sup>2</sup> Phys. Rev. 8, 38. (1899).

<sup>3</sup> Wied. Ann. 69, 140. (1899).

<sup>4</sup> Jour. phys. Chem. June (1901).

<sup>5</sup> Ber. d. Deutsch. Chem. Gesel. 32, 2342, (1899). Zeit. anorg. Chem. 25, 209. (1900).

<sup>6</sup> Zeit. phys. Chem. 23; 267. (1897). See also Wied. Ann. 55, 633. (1835); 58, 1; 59, 17 (1896); 60, 28, 500, (1897).

the apparatus employed. The reader is referred to Drude's original articles, after reading which the additional remarks on the method contained in the paragraphs that now follow will be much better understood.

The apparatus used for these measurements was a trifle larger than the one described by Drude. The wave-length of the electrical waves in the two parallel wires in air was about 84 cm. as compared with 74 cm. of the apparatus employed by Drude. A vacuum tube containing hydrogen was used to determine the settings for maximum resonance. It served very well indeed for this purpose.

Of the two methods described by Drude the first is the more accurate, but it necessitates the use of comparatively large quantities of substance, at least 200 cc, which, in most cases, were not available. Moreover, the poisonous nature of many of the compounds made it desirable to work with small quantities which could be kept in a closed cell while under investigation. Drude's "second" method, although less accurate, was therefore chosen. This method enables one to operate with less than a cubic centimeter of solvent and gives results accurate to within two per cent. In this method the substance to be measured is introduced into a small condenser which is placed in the secondary circuit. The length of the secondary circuit is then adjusted for maximum resonance. The dielectric constant corresponding to the length noted is found from a calibration curve representing the results obtained in calibrating the apparatus for the particular condenser.

Four cells similar in form but of different capacities served as condensers. The apparatus was calibrated for each cell with the liquids recommended by Drude, namely: benzene, acetone, water, mixtures of benzene and acetone, and mixtures of acetone and water. Seventeen liquids whose dielectric constants range from 2.26 to 80.9 at 19° C. were prepared. The benzene used for these calibrating solutions was Kahlbaum's thiophene free preparation, purified by crystallization. Its boiling point was 79.2° C. under 744.6 mm of pressure. The acetone was like-

wise Kahlbaum's preparation—it was prepared from the bisulphite compound. It boiled at 55.7° C. under 746 mm of pressure. The water used had a specific conductivity of  $3.6 \times 10^{-6}$ .

In calibrating, the "zero" of the apparatus, obtained by placing a straight piece of copper wire in place of the cell, was frequently redetermined, as a change in the position of certain parts of the apparatus may produce a change of the "zero" point. This precaution was also taken whenever solvents of unknown dielectric constants were under examination. As a check on any change in the capacity of the cells, the calibrating liquids whose dielectric constants were nearest in value to that found for the solvent under examination were introduced into the cell and the settings for maximum resonance determined. In this way any change in the position of the condenser plates could be readily detected. This procedure also gives all the necessary data for calculating the dielectric constant according to the formula given by Drude:<sup>1</sup>

$$D = D_1 + (D_2 - D_1) \frac{\cot \frac{2\pi l}{\lambda} - \cot \frac{2\pi l_1}{\lambda}}{\cot \frac{2\pi l_2}{\lambda} - \cot \frac{2\pi l_1}{\lambda}}$$

in which  $\lambda$  is the wave-length of the electric waves in air,  $D$  is the dielectric constant sought,  $l$  is the setting for maximum resonance when the cell contains the solvent whose dielectric constant is sought;  $D_1$ ,  $l_1$  and  $D_2$ ,  $l_2$ , are the dielectric constants and settings of the calibrating solutions. In working with pyridine the dielectric constant was calculated by this formula using 84 cm for  $\lambda$ . The value found was the same as the value obtained with the aid of the calibration curve.

From 10 to 30 settings for maximum resonance were made for each solvent examined, and the average of these was the value used for obtaining the dielectric constant.

The methods of dehydrating and rectifying the various solvents will be found under the head of each particular solvent in the statement of results given below.

A series of trial experiments was at first made with the appa-

<sup>1</sup> Zeit. phys. Chem., 23, 309. (1897).

ratus in order to test it thoroughly. The dielectric constants of ethyl ether, chloroform, ethyl benzoate, salicylic aldehyde, benzonitrile, and nitrobenzene were measured, and the results obtained agreed very well with those given by Drude. It is therefore entirely superfluous to again report the numerical results obtained for these substances.

#### Experimental Results.

##### THE NITRILES.

The dielectric constants of the following aliphatic nitriles were measured: Hydrocyanic acid, acetonitrile, propionitrile, butyronitrile, iso-propyl cyanide, valeronitrile, iso-butyl cyanide, capronitrile, and ethylene cyanide. In the aromatic series, benzonitrile, benzyl cyanide, ortho-toluenitrile, mandelic nitrile, and  $\alpha$ - and  $\beta$ - naphthonitriles were measured.

*Hydrocyanic Acid.*—The sample of hydrocyanic acid used was prepared in the usual way by slowly adding a strong aqueous solution of potassium cyanide to sulphuric acid of Sp. Gr. 1.25 in a retort connected with a reflux condenser kept at 30° C. The gas was then dried at 30° C. by passing it through a series of three large U tubes, kept at 30° C., and containing fused calcium chloride. The gas was condensed in a tube provided with glass stopcocks, suspended in a bath at 0°. A colorless liquid was thus obtained which left no residue upon evaporation. Some of the liquid was introduced into the cell adapted for the measurement of liquids having a high dielectric constant. The cell was securely stoppered and the measurements were made at 21° C. No appreciable absorption was observed, the position for maximum resonance being about as well defined as in the case of acetone. The D. C.<sup>1</sup> found is higher than the D. C. of water. This necessitated an extrapolation of the calibration curve in order to get an approximate value. The D. C. obtained in this way is  $95.0 \pm 3.5$ . After this exceedingly high result had been obtained a second sample of hydrocyanic

<sup>1</sup> The abbreviation D. C. is used for dielectric constant in the presentation of the results.

acid was prepared by redistilling the first sample from a water-bath kept at 30° C. The gas was again passed through the drying tubes and condensed as before. Measurements with this sample gave the same readings for maximum resonance as in the first case. The temperature coefficient is negative, but it was not accurately determined.

*Acetonitrile*.—The sample of acetonitrile first measured was obtained by distilling a sample of Kahlbaum's make. Its boiling point was very constant, being 80.9° C. under a pressure of 745 mm.. The average of four determinations gave the value 36.5 for the D. C. at 21° C.

A second sample, prepared by Prof. Kahlenberg from the Kahlbaum preparation by dehydrating it with phosphorus pentoxide, and redistilling twice, was measured. Its boiling point was 80.7 under a pressure of 749 mm. The measurements were made at 22° and gave the same result as was obtained with the first sample.

A third sample, also furnished by Prof. Kahlenberg, was finally measured. This sample was twice dehydrated with larger quantities of phosphorus pentoxide than were used in the previous case, and was distilled from phosphorus pentoxide. It had a boiling point of 80.2° C. under a pressure of 736 mm. The D. C. was calculated by the formula previously given, and found to be 36.1 at 21° C.

*Propionitrile*.—This sample was Schuchardt's preparation. Its boiling point was 94.6° under a pressure of 749 mm. The average of four determinations at different times gave the value 26.5 for the D. C. at 22° C. The absorption was slight.

*Butyronitrile*.—The sample tested was Schuchardt's preparation. It was redistilled from calcium chloride. Its boiling point was 116.5° to 118° C. under 742 mm of pressure. The average of three different determinations is 20.3 at 21° C.

*Iso-propylcyanide*.—The sample was Schuchardt's preparation. It was dehydrated with calcium chloride and redistilled. Its boiling point was 106°–107° C. under 744 mm of pressure.

The average of three determinations gave the value 20.4 for its D. C. at 24° C.

*Valeronitrile* (normal).—The sample was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion which distilled between 137° and 139° C., under 743 mm of pressure was taken for the measurements. The D. C. was found to be 17.4° at 31° C.

*Iso-butylcyanide*.—The sample was Schuchardt's make; it was redistilled from calcium chloride, and the portion distilling between 129° and 130.5° C., under a pressure of 742 mm was taken for the measurements. Its D. C. was found to be 17.95 at 22° C.

*Capronitrile*.—The sample used was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion distilled between 153°–154.2° C., under 743 mm pressure, was taken for the measurements. Its D. C. was found to be 15.5 at 22° C. The higher members of the series show a slight amount of absorption, but the maximum resonance is still well enough defined without increasing the intensity of the oscillations in the secondary circuit.

*Ethylene Cyanide*.—The sample of succinic acid nitrile was of Schuchardt's make. It was treated with fused calcium chloride, filtered and redistilled twice under diminished pressure. Its boiling point was 168° C. under a pressure of 28 mm. A solid, almost colorless, amorphous compound was thus obtained which melted at 54° C. Its D. C. was measured in the form of cell used by Drude<sup>1</sup> for the measurement of substances at higher temperatures. During the measurements the cell was kept in an oil-bath of the form figured and described by Coolidge.<sup>2</sup> The bath was attached to the ebonite slide by means of a small spring clamp. The temperature was kept at 60° ± 1° during the measurements of the liquid ethylene cyanide. The average of three determinations gave the value 61.2 for its D. C. The D. C. of the solid compound was also determined. Three determi-

<sup>1</sup> See Fig. 7, p. 225, *Zeit. phys. Chem.* 23. (1897).

<sup>2</sup> *Wied. Ann.* 69, 133. (1899).

nations averaged 65.3 at 23° C. No sudden change in the D. C. was observed at the melting point. The absorption of the solid ethylene cyanide was very slight; but the liquid sample did not show a well defined maximum, which was found to be due to its greater conductivity. The qualitative measurements of its resistance show that the temperature has a great influence on the resistance. At room temperatures the resistance is about twenty times as great as it is at 60° C.; but no sudden change in the resistance was observed at the melting point.

*Toluenitrile* (ortho).—Schuchardt's preparation was redistilled from calcium chloride. A straw colored distillate, boiling at 200° — 201° C. under a pressure of 733 mm. was thus obtained. Its D. C. was found to be 18.5 at 23° C. It showed slight absorption.

*α-Naphthonitrile*.—Schuchardt's preparation was redistilled under diminished pressure. Its melting point was 37° C.; but it is easily kept in a liquid state at 20° C. when the solid phase is not present. Its dielectric constant was determined in the form of cell adapted for measurements at higher temperatures, and the following values were found for the liquid sample.

D. C. = 16.0 at 70° C.

D. C. = 17.9 at 42° C.

D. C. = 19.2 at 22° C.

The position for maximum resonance was about as well defined as for nitro-benzene whose absorption index Drude<sup>1</sup> places at 0.05. The D. C. of the solid sample was found to be 6.3 at 21° C.; but this value is only approximate, for the position for maximum resonance was not well defined.

*β-Naphthonitrile*.—The sample used for the measurements was obtained by distilling Schuchardt's preparation under diminished pressure. Its boiling point was 190° C. under 35 mm. of pressure, and its melting point was 64° C. The D. C. of the liquid was found to be 16.9 at 70° C., and for the solid the value 4.3 at 23° C. was obtained, the position for maximum resonance being well defined in both the solid and the liquid samples.

<sup>1</sup> Zeit. phys. Chem. 23, 309. (1897).



*Mandelic Nitrile*.—The preparation from which the sample was obtained was of Schuchardt's manufacture. It showed decided signs of decomposition, being of a dark brown color and somewhat syrupy. It was dehydrated with fused calcium chloride, was filtered and distilled under diminished pressure, and the sample thus obtained was redistilled. Its boiling point was  $94^{\circ}$  C. under a pressure of 50 mm. A mobile, colorless liquid was thus obtained whose specific conductivity was found to be  $2.2 \times 10^{-10}$  reciprocal ohms. Its dielectric constant was found to be 17.82 at  $23^{\circ}$  C. An absorption of about the same order as that of nitrobenzene was observed. Its absorption index was also determined by the method outlined by Drude.<sup>1</sup> The value obtained in this way was .045, which agrees very well with that of nitrobenzene which Drude places at .05. Drude has found that this anomalous absorption is characteristic of compounds containing hydroxyl.

#### THE SUBSTITUTED AMMONIAS.

The amines whose dielectric constants were measured are enumerated in Table III. The samples used were Schuchardt's preparations with the exception of the two toluidines and the xylydine which were of Trommsdorff's manufacture. Each sample, except methylamine, was dehydrated with fused potassium hydroxide and then distilled; and in many cases the distillate was again treated with fused potash and redistilled. The sample of methylamine was doubtless impure for, upon evaporation it left a residue, and it did not yield a well defined position for maximum resonance, while with all the other samples well defined maxima were observed. Hence the value found for the D. C. of methylamine is doubtless too high.

The third column in the following table gives the boiling point of the samples taken for the measurements, and the fourth column indicates the corresponding barometric pressure, while the last column gives the temperature at which the D. C. was measured.

<sup>1</sup> Zeit. phys. Chem. 23, pp. 292-297. (1897).

TABLE III.

Name.	Formula.	B. P.	P.	D. C.	t°C
Methylamine .....	$\text{CH}_3 \text{NH}_2$	.....	.....	< 10.5	21
Ethylamine.....	$\text{C}_2\text{H}_5 \text{NH}_2$	< 17.5	752	6.17	21
Iso-propylamine .....	$\begin{Bmatrix} \text{CH}_3 \\ \text{CH}_3 \end{Bmatrix} \text{CH NH}_2$	36	750	5.45	20
Butylamine (n).....	$\text{C}_4 \text{H}_9 \text{NH}_2$	76-77	740	5.30	21
Iso-butylamine .....	$\begin{Bmatrix} \text{CH}_3 \\ \text{CH}_3 \end{Bmatrix} \text{CH. CH}_2 \text{NH}_2$	68	745.2	4.43	21
Amylamine .....	$\text{C}_5 \text{H}_{11} \text{NH}_2$	94-95	740.4	4.50	22
Di-ethylamine .....	$(\text{C}_2 \text{H}_5)_2 \text{NH}$	54.5	733.4	3.58	21
Di-propylamine .....	$(\text{C}_3 \text{H}_7)_2 \text{NH}$	108-108.5	745.5	2.90	22
Di-iso-butylamine .....	$(\text{C}_4 \text{H}_9)_2 \text{NH}$	134.5	735	2.65	22
Trimethylamine .....	$\text{N}(\text{CH}_3)_3$	< 8°	750	2.95	4
Aniline.....	$\text{C}_6 \text{H}_5 \text{NH}_2$	179.4	741	7.2	19
Toluidine (o).....	$\text{C}_6 \text{H}_4 \begin{Bmatrix} \text{NH}_2 (1) \\ \text{CH}_3 (2) \end{Bmatrix}$	194.5	738	5.93	20
Toluidine (m) .....	$\text{C}_6 \text{H}_4 \begin{Bmatrix} \text{NH}_2 (1) \\ \text{CH}_3 (3) \end{Bmatrix}$	194.2	738.2	5.95	20
Xylidine 1:3:4.....	$\text{C}_6 \text{H}_3 \begin{Bmatrix} \text{CH}_3 1 \\ \text{CH}_3 3 \\ \text{NH}_2 4 \end{Bmatrix}$	209.5	737.0	4.90	20
Mono-methylaniline.....	$\text{C}_6 \text{H}_5 \text{NHCH}_3$	189.4	740.5	5.8	20
Di-methylaniline .....	$\text{C}_6 \text{H}_5 \text{N}(\text{CH}_3)_2$	191.5	735	5.07	20
Di-benzylamine.....	$(\text{C}_7 \text{H}_7)_2 \text{NH}$	200	40	3.55	20

## MISCELLANEOUS ORGANIC COMPOUNDS.

*Pyridine*.—The sample was Schuchardt's preparation. It was redistilled and found to boil from 115.5° to 117° C. under 745 mm. of pressure. With this several measurements were made, the average of the results for the D. C. being 12.35 at 21° C.

A second sample was furnished by Prof. Kahlenberg. Kahlbaum's best preparation was carefully purified according to the method given by Ladenburg.<sup>1</sup> The portion boiling at 114° C.

<sup>1</sup> Liebig Ann. 247, 1. (1888).

under 744.6 mm. of pressure was used for the measurements. The D. C. was found to be 12.55 at 20° C., a result which agrees well with the foregoing. The settings for maximum resonance were well defined.

*α-Picoline.*—The sample was Schuchardt's preparation. It was treated with fused calcium chloride, and redistilled. The boiling point of the portion taken for the measurements was 128.5° — 129.5° C. at 736 mm. of pressure. The value found for the D. C. is 9.8 at 20° C.

The unpurified sample of pyridine, it will be noted, gave a slightly lower D. C. than the purified sample. The former very likely contained a slight amount of picoline.

*Quinoline.*—Two samples of quinoline were measured. The first was obtained by redistilling Schuchardt's preparation marked, "Quinoline from Coal Tar." The portion which distilled at 232° C. under 746 mm. of pressure was measured. Its D. C. was found to be 8.7 at 22° C.

The second sample was a synthetic preparation, made by Messrs. Maxon and Thomas in this laboratory according to the method of Skraup. The boiling point of the sample measured was 232° C. under 746 mm. of pressure. Its dielectric constant was found to be 8.9 at 20.5° C. The agreement is close enough to fall within the limit of error. The absorption is slight. These values of the D. C. agree well with the result, 8.9, obtained by Turner<sup>1</sup> who worked with Nernst's apparatus.

*Piperidine.*—The sample was E. de Haën's preparation. It was redistilled and the portion distilling between 105.5° and 107.0° C. under a pressure of 745 mm. was used for the measurements. It was an almost colorless liquid and showed no absorption. The value found for its D. C. was 5.8 at 22° C.

*Carbon dichloride.*—The sample was of Schuchardt's make. Its boiling-point was 118° at 726.5 mm. of pressure. The value 2.46 was found for its D. C. at 21° C.

*Nitromethane.*—Schuchardt's preparation was treated with fused calcium chloride and redistilled. Its boiling-point was

<sup>1</sup> Zeits. phys. Chem. 35, 385. (1900).

99.9° under a pressure of 738.4 mm. The dielectric constant found was 40.4 at 19° C. Thwing<sup>1</sup> gives the value 56.36 at 15° C.

*Nitroethane*.—Schuchardt's preparation was dehydrated and rectified as in the case of nitromethane. Its boiling-point was 110.5° C. at 738.3 mm. of pressure. The value of its D. C. was found to be 29.5 at 18° C.

*Methyl Nitrate*.—The sample of methyl nitrate used for the measurements was prepared from Kahlbaum's best methyl alcohol by treating it with nitric acid according to the method of J. Lea.<sup>2</sup> The sample was washed with water containing a small amount of sodium carbonate, and was dehydrated with fused calcium chloride and finally distilled from a waterbath. Its boiling point was 64.4° C. at 730.2 mm. of pressure. The value 23.5 was found for its D. C. at 18° C. No absorption was observed.

*Ethyl Nitrate*.—Schuchardt's preparation was washed with water containing a trace of sodium carbonate to remove traces of nitric acid and alcohol. It was then dried with fused calcium chloride and redistilled twice. The boiling point was 86.1° at 729.4 mm. of pressure. The average of three determinations gave the value 18.3 at 18° C. Thwing found the value 17.72 at 15° and Drude found 19.6 for the D. C. of this compound at 17° C.

*Propyl Nitrate*.—This compound was prepared according to the method of Wallach and Schulze.<sup>3</sup> The propyl alcohol used for its preparation was redistilled. Its boiling-point was 95.8° under a pressure of 752 mm. The sample of propyl nitrate was dehydrated and rectified as described for ethyl nitrate. Its boiling point was 108.5° C. under a pressure of 738.5 mm. The value 13.9 was obtained for its D. C. at 18° C.

*Iso-butyl Nitrate*.—Schuchardt's preparation was redistilled. Its boiling-point was 120.0° under 738.2 mm. of pressure.

<sup>1</sup> Physical Review, 2, 35. (1894).

<sup>2</sup> See Beilstein, Handbuch der Organischen Chemie. (Third edition) Vol. I, p. 324.

<sup>3</sup> Ber. d. Deutsch. Chem. Gesel. 14, 422.

One series of measurements was made which gave the value 11.7 for its D. C. at 19° C.

*Iso-propyl Nitrite*.—A sample of iso-propyl nitrite, probably not entirely free from nitrous acid, was measured. The value 11.5 was found for its D. C. at 19° C.

*Ethyl Urethane*.—The sample used for the measurements was kindly furnished by the School of Pharmacy of this University. Its melting-point was 48° C. The value found for the D. C. of the liquid compound at 60° was 13.6; the solid form gave the value 3.18 at 23° C.

*Amylsulph-hydrate*.—The boiling point of the sample was 116.5° C. under 752 mm. of pressure. The D. C. found was 4.35 at 22° C.

#### INORGANIC SOLVENTS.

*Phosphorus Trichloride*.—The sample used was of Kahlbaum's manufacture. It was redistilled, boiling at 74.1° C. under a pressure of 740 mm. The average of two determinations gave the value 3.36 for its D. C. at 22° C. No absorption was observed.

*Arsenic Trichloride*.—The sample which served for the measurements had been prepared in this laboratory by Dr. Lincoln. It was dried with fused calcium chloride and was redistilled. The sample used boiled from 127° — 128° C. under 740 mm. of pressure. The value 12.35 was obtained for its D. C. at 21° C. Slight absorption which was doubtless due to conduction was observed.

*Antimony Trichloride*.—The sample used for the measurements conducted about as well in the fused state, at 70° C., as a fiftieth normal sodium chloride solution. The position for maximum resonance was still well enough defined without increasing the intensity of the oscillations in the secondary circuit, but the absorption was more marked than with arsenic trichloride. Hence it seemed advisable to determine the D. C. by the method outlined by Drude<sup>1</sup> for substances which show absorp-

<sup>1</sup> See Drude Zeit. phys. Chem. 23, pp. 294-297.

tion. The value thus obtained was 33.2 at 75° C. For the solid compound the value 5.4 was found at 18° C.

*Antimony Pentachloride.*—The sample used was E. de Haën's preparation. It was found securely stoppered and hence was not rectified. The value 3.78 was obtained for its D. C. at 21.5° C.

*Stannic chloride.*—Kahlbaum's preparation was redistilled. Its boiling-point was 117.5° C. under 750 mm. of pressure. The value found for its D. C. is 3.2 at 22° C.

*Sulphur Mono-chloride.*—The sample used for the measurements had been prepared in this laboratory by Mr. Harry Eggers. It was redistilled and found to boil at 136.2° under 738 mm. of pressure. The value 4.8 was found for its D. C. at 22° C.

*Sulphur Trioxide.*—A sample of Kahlbaum's sulphur trioxide was measured in both the solid and liquid states. The value 3.56 was obtained for the D. C. of the liquid sample at 21°, and 3.64 for the solid at 19° C.

*Phosphorus Oxychloride.*—The sample used for the measurements was prepared according to the method described by Gerhardt.<sup>1</sup> About 150g of phosphorus pentachloride was mixed with one-half its weight of dry oxalic acid in a retort and heated gently. The distillate thus obtained was redistilled and found to boil at 105.1° under a pressure of 739.2 mm. The value obtained for its D. C. was 13.9 at 22° C.

*Sulphurylchloride* ( $\text{SO}_2\text{Cl}_2$ ).—This compound was prepared by the method of Schulze.<sup>2</sup> A quality of camphor was liquefied by passing dry sulphur dioxide into the containing vessel. Dry chlorine gas was then passed into the liquid and the current of sulphur dioxide was also continued. In the presence of the camphor chlorine and sulphur dioxide unite to form sulphuryl-chloride. After several distillations a product boiling at 68.4° under 740.2 mm. of pressure was obtained. The value 9.15 was found for its D. C. at 22° C.

<sup>1</sup> Ann. Chim. et de Phys. [3] 44, 102.

<sup>2</sup> Jour. prakt. Chem. 23, 331.

*Thionyl chloride* ( $\text{SOCl}_2$ ).—The sample used for the measurements was prepared in the usual way, namely, by the reaction of dry  $\text{PCl}_5$  with dry  $\text{SO}_2$ . [ $\text{PCl}_5 + \text{SO}_2 = \text{POCl}_3 + \text{SOCl}_2$ ]. About 150g of  $\text{PCl}_5$  was placed in a retort connected with a reflux condenser and a stream of  $\text{SO}_2$  was conducted in till the  $\text{PCl}_5$  had become liquefied; another portion of  $\text{PCl}_5$  was then added, and the stream of  $\text{SO}_2$  was continued. The liquid thus obtained was heated for some time, with the return condenser still attached, to free it from  $\text{SO}_2$ ; and finally, by repeated fractional distillation a sample of  $\text{SOCl}_2$  was obtained which had a constant boiling point of  $76.8^\circ$  under a pressure of 751.3 mm. The value found for its D. C. is 9.05 at  $22^\circ \text{C}$ . Slight absorption was observed.

*Liquid Sulphur Dioxide*.—A sample of liquid sulphur dioxide was measured in a sealed cell. The value found for its D. C. at  $22^\circ$  is 12.35. Linde,<sup>1</sup> by Nernst's method, found the value 14.8 at  $23^\circ$ , while Coolidge<sup>2</sup> found the value 13.75 at  $14.5^\circ$ . I made but one determination.

*Bromine*.—The sample of bromine used for the measurements was prepared by Miss Winifred Titus from potassium bromide, potassium bromate, and sulphuric acid according to the method of J. S. Stas.<sup>3</sup> The value 3.18 was obtained for its D. C. at  $23^\circ \text{C}$ . The measurements were made soon after the bromine had been introduced into the cell, so as to minimize the action of the bromine on the platinum plates.

*Iodine*.—Pure resublimed iodine obtained from the chemical works of de Haën at List near Hannover was once more sublimed by Prof. Kahlenberg. An attempt was made to determine its D. C. in the solid and the liquid states in a sealed cell. With the solid sample the position for maximum resonance was still fairly well defined, but after removing the iodine from the cell it was found, that the plates of the condenser were covered with a black coating, which doubtless introduced an error. Hence

<sup>1</sup> Wied. Ann. 56, 546. (1895).

<sup>2</sup> Wied. Ann. 69, 130. (1899).

<sup>3</sup> Unters. über Proport. u. Atomg. Leipzig, 1867, p. 220. See also Fehling's Handwörterbuch d. Chemie. I, p. 235.

the value 10.3, which was found for its D. C. at 23°, must be regarded as only approximate. With the liquid sample no distinct maximum resonance was obtained.

*Cyanogen* (Liquid).—In view of the high dielectric constant obtained for hydrocyanic acid it seemed of special interest to determine the D. C. of liquid cyanogen. Prof. Kahlenberg kindly offered to undertake the preparation of this compound with me. We evolved the cyanogen by treating a strong solution of copper sulphate with a concentrated solution of potassium cyanide. The gas was dried by passing it through two large U-tubes filled with fused calcium chloride. It was condensed by means of solid carbonic acid. The D. C. was measured in a sealed cell at 23° C. We found the value 2.52, the position for maximum resonance being well defined.

All the foregoing results are summarized in the following table, in which the abbreviations (l.) and (s.) are used for liquid and solid respectively.

TABLE IV.

Name.	Formula.	t.	D. C.
Cyanogen (l.).....	(CN) <sub>2</sub>	23	2.52
Hydrocyanic acid (l.).....	HCN	21	95.
Acetonitrile.....	CH <sub>3</sub> CN	21	36.4
Propionitrile.....	C <sub>2</sub> H <sub>5</sub> CN	22	26.5
Butyronitrile (n).....	C <sub>3</sub> H <sub>7</sub> CN	21	20.3
Iso-propyl cyanide.....	(CH <sub>3</sub> ) <sub>2</sub> CH CN	24	20.4
Valeronitrile (n).....	C <sub>4</sub> H <sub>9</sub> CN	21	17.4
Iso-butyl cyanide.....	(CH <sub>3</sub> ) <sub>2</sub> CH CH <sub>2</sub> CN	22	17.95
Capronitrile.....	(CH <sub>3</sub> ) <sub>2</sub> CH CH <sub>2</sub> CH <sub>2</sub> CN	22	15.5
Ethylene cyanide (s).....	C <sub>2</sub> H <sub>4</sub> (CN) <sub>2</sub>	23	65.3
Ethylene cyanide (l).....	C <sub>2</sub> H <sub>4</sub> (CN) <sub>2</sub>	60	61.2
α-Naphthonitrile (s).....	C <sub>10</sub> H <sub>7</sub> CN	21	63.7
α-Naphthonitrile (l).....	C <sub>10</sub> H <sub>7</sub> CN	42	17.9
α-Naphthonitrile (l).....	C <sub>10</sub> H <sub>7</sub> CN	70	16.0
β-Naphthonitrile (s).....	C <sub>10</sub> H <sub>7</sub> CN	21	4.3
β-Naphthonitrile (l).....	C <sub>10</sub> H <sub>7</sub> CN	70	16.9
Mandelic nitrile.....	C <sub>6</sub> H <sub>5</sub> CH OH CN	23	17.82



TABLE IV—Continued.

Name.	Formula.	t.	D. C.
Benzonitrile <sup>1)</sup> .....	$C_6 H_5 CN$	21	26.0
Benzyl cyanide <sup>2)</sup> .....	$C_6 H_5 CH_2 CN$	21	14.9
Toluenitrile (ortho) .....	$C_6 H_4 \left\{ \begin{smallmatrix} CH_3 \\ CN \end{smallmatrix} \right\}$	23°	18.4
Pyridine .....	$C_5 H_5 N$	21	12.4
$\alpha$ -Picoline .....	$C_5 H_4 NCH_2 (\alpha)$	20	9.8
Piperidine .....	$C_5 H_{10} NH$	22	5.8
Quinoline <sup>3)</sup> .....	$C_9 H_7 N$	21	8.8
Carbon dichloride .....	$C_2 Cl_4$	21	2.46
Ethyl sulph-hydrate .....	$C_2 H_5 SH$	22	4.35
Ethyl urethane (s) .....	$CO. NH_2. O. C_2 H_5$	23	3.18
Ethyl urethane (l) .....	$CO. NH_2. O. C_2 H_5$	60	18.6
Methylamine .....	$CH_3 NH_2$	21	<sup>4)</sup> 10.5
Ethylamine .....	$C_2 H_5 NH_2$	21	6.17
Iso-propylamine .....	$(CH_3)_2 CH NH_2$	20	5.45
Butylamine (n) .....	$C_4 H_9 NH_2$	21	5.30
Isobutylamine .....	$(CH_3)_2 CH CH_2 NH_2$	21	4.43
Amylamine .....	$C_5 H_{11} NH_2$	22	4.50
Diethylamine .....	$(C_2 H_5)_2 NH$	21	3.58
Dipropylamine .....	$(C_3 H_7)_2 NH$	22	2.90
Di-isobutylamine .....	$[(CH_3)_2 CH CH_2]_2 NH$	22	2.65
Trimethylamine .....	$(CH_3)_3 N$	24	2.95
Aniline <sup>4)</sup> .....	$C_6 H_5 NH_2$	20	7.20
Toluidine (ortho) .....	$C_6 H_4 \left\{ \begin{smallmatrix} NH_2 \\ CH_3 (o) \end{smallmatrix} \right\}$	20	5.93
Toluidine (meta) .....	$C_6 H_4 \left\{ \begin{smallmatrix} NH_2 \\ CH_3 (m) \end{smallmatrix} \right\}$	20	5.96
Xylidine 1:3:4 .....	$C_6 H_3 \left\{ \begin{smallmatrix} CH_3-1 \\ CH_3-3 \\ NH_2-4 \end{smallmatrix} \right\}$	20	4.90
Monomethylaniline .....	$C_6 H_5 NH CH_3$	20	5.8
Dimethylaniline .....	$C_6 H_5 N (CH_3)_2$	20	5.07
Dibenzylamine .....	$(C_6 H_5)_2 NH$	20	3.55
Nitromethane <sup>5)</sup> .....	$CH_3 NO_2$	19	40.4
Nitroethane .....	$C_2 H_5 NO_2$	18	29.5
Methylnitrate .....	$CH_3 NO_3$	18	23.5

<sup>1)</sup> Drude found 26.0 for the D. C. of benzonitrile at 21°C.

<sup>2)</sup> Drude found 15.0 for the D. C. of benzylcyanide at 19°C.

<sup>3)</sup> Turner found 8.9 for quinoline.

<sup>4)</sup> The value 7.15 (at 21°) was found by Drude; and 7.22 (at 15°) by Ratz. Zeit. phys. Chem. 19, 94. (1896).

<sup>5)</sup> Thwing gives the value 56.36 at 15°.

TABLE IV — Continued.

Name.	Formula.	t.	D. C.
Ethylnitrate .....	$C_2 H_5 NO_2$	18	18.8
Propylnitrate .....	$C_3 H_7 NO_2$	18	18.9
Isobutylnitrate .....	$(CH_3)_2 CH CH_2 NO_2$	19	11.7
Isopropylnitrite .....	$(CH_3)_2 CH NO_2$	19	11.57
Phosphorus trichloride .....	$P Cl_3$	22	3.36
Arsenic trichloride .....	$As Cl_3$	21	12.35
Antimony trichloride (s) .....	$Sb Cl_3$	18	5.4
Antimony trichloride (l) .....	$Sb Cl_3$	75	33.2
Stannic chloride .....	$Sn Cl_4$	22	3.2
Antimony pentachloride .....	$Sb Cl_5$	21.5	3.78
Sulphur monochloride .....	$S_2 Cl_2$	22	4.8
Sulphur trioxide (s) .....	$(SO_2)_2$	19	3.64
Sulphur trioxide (l) .....	$(SO_2)_2$	22	3.56
Sulphurylchloride .....	$SO_2 Cl_2$	22	9.15
Thionylchloride .....	$SO Cl_2$	22	9.05
Phosphorus oxychloride .....	$PO Cl_3$	22	13.09
Sulphur dioxide (l) <sup>1</sup> .....	$SO_2$	22	12.35
Bromine (l) .....	Br	23	3.13
Iodine (s) .....	I.	23	10.37

The results obtained with the aliphatic nitriles the primary amines, and the nitrates are represented graphically in Curves I, IV and V of the accompanying figure. The dielectric constants are plotted as ordinates, and the members of the homologous series are noted as abscissæ, a definite distance being chosen for each addition of  $CH_2$ . Curve II represents Drude's<sup>2</sup> values for the dielectric constants of the alcohols, while curve II (a) presents approximately the values obtained by Thwing,<sup>3</sup> Nernst<sup>4</sup> and Tereschin<sup>5</sup> for the dielectric constants of the alcohols. Curve III represents the values obtained by Drude for the dielectric constants of the fatty acids. Hence in Curve I, R rep-

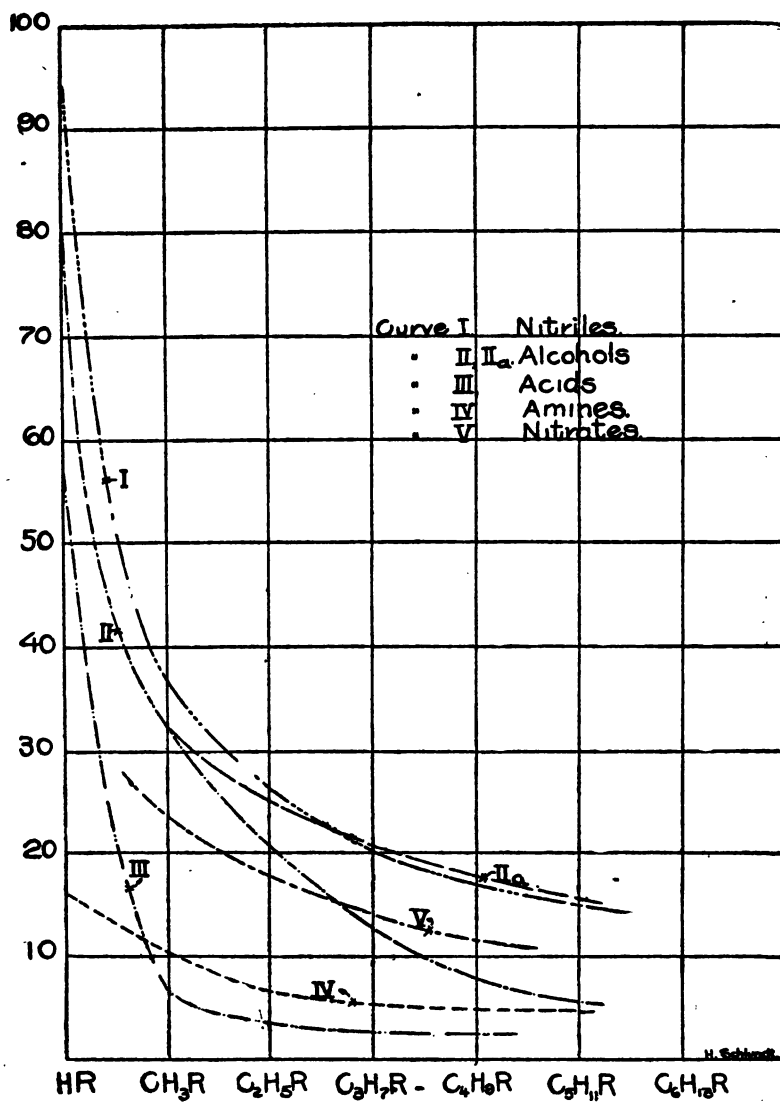
<sup>1</sup> Linde gives the value 14.8 at 23°. Coolidge gives the value 13.75 at 14.5.

<sup>2</sup> Zeit. phys. Chem. 23, 309, (1897).

<sup>3</sup> Zeit. phys. Chem. 14, 286, (1894).

<sup>4</sup> Zeit. phys. Chem. 14, 622, (1894).

<sup>5</sup> Wied. Ann. 36, 792, (1889).



resents the cyanogen group (CN); in Curves II and IIa, R represents the hydroxyl group (OH); in Curve III, it represents the carboxyl group (COOH); in Curve IV the amido group ( $\text{NH}_2$ ); while in Curve V, R represents the ( $\text{NO}_2$ ) group. The value 16.2 for the dielectric constant of liquid ammonia is taken from the work of Coolidge<sup>1</sup> who measured its dielectric constant at 14° C.

#### Discussion of Results.

The marked differences that exist between the physical properties of the first two members of any homologous series of compounds are well exemplified by the great differences between the dielectric constants of hydrocyanic acid and acetonitrile, of water and methyl alcohol and of formic acid and acetic acid. The difference in value between the dielectric constants of liquid ammonia and liquid methylamine is not so marked as in the other cases just mentioned; but it is highly probable that the value found for methylamine is too high. The curves show that in an homologous series the dielectric constants decrease with increase of molecular weight. This also holds for the aromatic amido compounds. Pyridine (D. C., 12.4) and  $\alpha$ -picoline (D. C., 9.8) also illustrate this fact, as do also nitrobenzene [D. C., 35.0] and ortho-nitrotoluene [D. C., 27.]<sup>2</sup> The primary amines have higher values for their dielectric constants than the corresponding secondary amines, and the values for the secondary amines are higher than the tertiary, as is shown by the following examples:

Ethylamine, D. C. = 6.17.

Diethylamine, D. C. = 3.58.

Trimethylamine, D. C. = 2.95.

A further inspection of the values of the dielectric constants of the several homologous series of liquid compounds investigated by other observers will show that a decrease in the value of the dielectric constant with increase of molecular weight is

<sup>1</sup> Wied. Ann. 69, 130, (1899).

<sup>2</sup> This value was found by Turner. Zeit. phys. Chem. 35, 385, (1900).

the general rule. Tereschin<sup>1</sup> first pointed out this fact in connection with the values he obtained for the dielectric constants of a number of homologous esters of the aliphatic acids and of benzoic acids. The values obtained by Tomaszewski,<sup>2</sup> however, for the dielectric constants of the homologues of benzene, show that their dielectric constants increase with increase of molecular weight. The dielectric constants of the homologues of benzene and a number of aliphatic hydrocarbons have been determined by Landolt and Jahn,<sup>3</sup> by Nernst,<sup>4</sup> and by others. Some of these results are given in the following table: The second column indicates the values of the dielectric constants obtained by Tomaszewski, the third column the values obtained by Landolt and Jahn, while the last column gives the values obtained by Nernst.

TABLE V.

Substance.	D. C. (Tomaszewski).	D. C. (L.&J.).	D. C. (Nernst).
Benzene.....	2.218	2.222	2.255
Toluene.....	2.303	2.387	2.355
Xylene (ortho) .....		2.583	2.567
Xylene (meta) .....		2.35	2.372
Xylene (para) .....	2.333	2.245	2.251
Mesitylene.....		2.30	
Pseudocymenè.....		2.417	2.415
Cymenè.....	2.442	2.231	2.249
Benzene.....	2.218	2.222	2.255
Toluene.....	2.303	2.387	2.355
Ethylbenzene.....		2.414	2.424
Propylbenzene.....		2.351	2.380
Iso-propylbenzene.....		2.376	2.363
Iso-butylbenzene .....		2.341	2.347
Hexane.....		1.854	1.88
Octane.....		1.933	1.949
Decane.....		1.964	

<sup>1</sup> Wied. Ann. 36, p. 801, (1889).<sup>2</sup> Wied. Ann. 33, p. 41, (1898).<sup>3</sup> Zeit. phys. Chem. 10, 239, (1892).<sup>4</sup> Zeit. phys. Chem. 14, 622, (1894).

From the results of Landolt and Jahn and those of Nernst it appears that the dielectric constants at first increase with increase of molecular weight and subsequently they decrease as the molecular weight increases. Tomaszewski's values show an increase with increase of molecular weight throughout. Regardless of which series of values for the dielectric constants is correct, the results show that these hydrocarbons do not follow the rule observed in connection with most other homologous series of compounds,—namely, that an increase in molecular weight is accompanied by a decrease in the value of the dielectric constant.

The isomeric nitriles and alcohols have nearly the same dielectric constants, the iso-compounds showing slightly higher values. With the substituted ammonias the iso-compounds examined gave lower values than the normal compounds.

A comparison of the values of the dielectric constants of the alcohols and nitriles by means of Curves I and II shows that for oscillations of high frequency the nitriles have higher values throughout than the corresponding alcohols. For oscillations of low frequency the values for the dielectric constants of the higher members of the alcohol series are nearly the same as the values found for the corresponding nitriles with high frequency oscillations. [Compare curves IIa and I.] Since the nitriles show but slight absorption, their dielectric constants when examined by other methods where slower vibrations are used will probably agree closely with the values found with Drude's apparatus.

The marked effect of the presence of the cyanogen group in a compound upon the value of its dielectric constant, is further illustrated by comparing the dielectric constants of ethylacetate ( $\text{CH}_3 \text{COOC}_2 \text{H}_5$ ) and ethylecyanacetate ( $\text{CH}_2 \text{CNCO}_2 \text{C}_2 \text{H}_5$ ), for which Drude<sup>1</sup> found the values 5.85 and 26.7 respectively. The values 26.5 and 65.3 here found for ethylecyanide ( $\text{C}_2 \text{H}_5 \text{CN}$ ), and ethylene cyanide ( $\text{C}_2\text{H}_4(\text{CN})_2$ ), respectively also exemplify this effect in a striking manner. Cyanogen itself,

<sup>1</sup> Zeit. phys. Chem. pp. 308, 310, (1897).

however, has a very low dielectric constant, the value being intermediate between the values of chlorine and bromine. The dielectric constant of liquid chlorine was determined by Linde,<sup>1</sup> who found the value 1.93 at 14° C., and by Coolidge<sup>2</sup>, who obtained the value 1.87 at 14.3°. The values obtained for liquid cyanogen (Table V) and bromine are 2.52 and 3.18, respectively, at 23° C.

For the purpose of this discussion, the inorganic solvents whose dielectric constants were measured, are divided into two groups. One group contains the solvents whose dielectric constants range from three to five, while the other group contains the solvents whose dielectric constants range from nine to thirty-three.

D. C. 3—5.	D. C. 9—33.
Sulphur monochloride.	Arsenic trichloride.
Phosphorus trichloride.	Antimony trichloride.
Sulphur trioxide.	Phosphorus oxychloride.
Antimony pentachloride.	Sulphur dioxide.
Stannic chloride.	Sulphuryl chloride.
Bromine.	Thionyl chloride.

The ionizing power of these solvents has been investigated by Kahlenberg and Lincoln<sup>3</sup>, and more fully by Walden.<sup>4</sup> The electrical conductivity measurements of Walden show that the solvents with low dielectric constants yield solutions with tetraethylammonium iodide, which do not conduct well enough to make quantitative measurements profitable, while the other solvents with relatively higher dielectric constants yield solutions with the same salt and with other salts that conduct fairly well. (See Table II.) Here then we have a good illustration of the Nernst-Thomson rule, that the greater the dielectric constant of a solvent the greater is its dissociating power. The following

<sup>1</sup> Wied. Ann. 56, 546, (1896).

<sup>2</sup> Wied. Ann. 69, 123, (1899).

<sup>3</sup> Jour. phys. Chem. 3, 12, (1899).

<sup>4</sup> Berichte d. Deutsch. Chem. Gesell. 32, 2862, (1899). Zeit. anorg. Chem. 25, 209, (1900).

table gives the molecular conductivities at nearly corresponding dilutions of tetraethylammoniumiodide,  $[N(C_2H_5)_4I]$ , dissolved in the solvents noted. These results are taken from the work of Walden to which reference has already been made. The molecular conductivities in liquid  $SO_2$  were made at zero degrees; in the other solvents the conductivities were made at  $25^\circ C$ . The last column indicates the dielectric constants of the solvents.

TABLE VI.

Solvent.	V.	$U_v$ .	D. C.
$POCl_3$ .....	500	33.45	13.9
$AsCl_3$ .....	480	54.26	12.35
$SO_2Cl_2$ .....	500	19.59	9.15
$SOCl_2$ .....	514	25.50	9.05
$SO_2$ .....	181 <sup>1</sup>	126.9	13.5

In connection with the results presented in this table it may be noted that there is no such parallelism between dielectric constant and molecular conductivity as one would expect by the Nernst-Thomson rule.

The high dielectric constant found for hydrocyanic acid is of special interest from a theoretical point of view since by the Nernst-Thomson rule, this compound should possess extraordinary dissociating power. The qualitative tests which Prof. Kahlenberg and I have made, however, indicate that hydrocyanic acid does not possess dissociating power in a marked degree. A number of salts which yield excellent conducting solutions when dissolved in water, show comparatively feeble conduction when dissolved in hydrocyanic acid. Here then is a striking exception to the Nernst-Thomson rule. The quantitative measurements of the electrical conductivity of salts dissolved in hydrocyanic acid are now in progress in this laboratory and their publication will doubtless be awaited with considerable interest.

This is the highest dilution which Walden examined.



The high dielectric constants of the nitriles and alcohols show a marked contrast to the low dielectric constants of the substituted ammonias, which are of about the same order as the dielectric constant of chloroform [D. C. = 5.0], and ether [D. C. = 4.4]. Now the ionizing power of chloroform and ether is exceedingly small, which fact is in perfect accord with the Nernst-Thomson rule. But Prof. Kahlenberg<sup>1</sup> finds that the primary amines, which have values for their dielectric constants approximately the same as those of chloroform and ether, still yield solutions that conduct fairly well. Here then we have a number of exceptions to the Nernst-Thomson rule opposite in kind to the case of solutions in hydrocyanic acid; namely, solvents with relatively very low dielectric constants that still possess moderate ionizing power.

The electrical conductivity of solutions in nitriles has been studied by Dutoit and Friderich.<sup>2</sup> Their results show that the conductivity of salts dissolved in the homologues, acetonitrile, propionitrile, and butyronitrile decreases in the order in which the solvents are named. Their dielectric constants also decrease in the same order; thus supporting the Nernst-Thomson rule. This relation between the dielectric constant and electrical conductivity is illustrated by the following table, in which U stands for the molecular conductivity at 25° C., and V, the number of liters in which one gram molecule of silver nitrate is dissolved.

TABLE VII.

Solvent.	V.	U.	D. C. at 21°.
Acetonitrile .....	64.0	103.7	36.4
Propionitrile .....	63.7	46.0	26.5
Butyronitrile .....	75.6	25.4	20.3

Propionitrile and benzonitrile have about the same dielectric constant, but the molecular conductivities of silver nitrate dis-

<sup>1</sup> Jour. phys. Chem. June, 1901.

<sup>2</sup> Bull. Chem. Soc. Paris [3] 19, 321, (1898).

solved in these nitriles are quite different, as a comparison of the results in the following table shows. The molecular conductivities of silver nitrate in benzonitrile are taken from the work of Lincoln<sup>1</sup> while those for the propionitrile are taken from the work of Dutoit and Friderich.<sup>2</sup>

TABLE VIII.

BENZONITRILE.		PROPIONITRILE.	
V.	U at 25°C.	V.	U at 25°C.
24.06	7.66	32.0	34.9
58.98	11.19	68.7	46.0
83.92	18.41		

The molecular conductivities of silver nitrate dissolved in pyridine and in butyronitrile furnish another interesting comparison.

TABLE IX.

Solvent.	V.	U. at 25°C.	D. C.
Butyronitrile <sup>3</sup> ).....	75.6	25.4	20.3
	150.4	32.1	.....
Pyridine <sup>4</sup> ).....	60.9	30.17	12.4
	140.7	36.21	.....

While Table VII shows that the Nernst-Thomson rule holds for the three members of the same homologous series, Table VIII demonstrates that chemically analogous substances having about the same dielectric constants may nevertheless yield solutions (containing the same solute) with very different electrical conductivities. Table IX shows conclusively that a pyridine solution of silver nitrate conducts better than a corresponding

<sup>1</sup> l. c. pp. 422, 423.<sup>2</sup> l. c. pp. 300, 331.<sup>3</sup> l. c. pp. 422, 423.<sup>4</sup> l. c. pp. 330, 331.

one in butyronitrile, notwithstanding the fact that the dielectric constant of pyridine is only 61% of that of butyronitrile. Here, then, we have two further exceptions to the Nernst-Thomson rule. But in these cases the exceptions might be explained on the basis of the theory of electrolytic dissociation. Since the molecular conductivity depends upon the speed of the ions as well as the number of ions, i. e., the degree of dissociation, it might be argued that the magnitude of the conductivity at corresponding dilutions, giving as it does the combined effect of these two factors, is therefore not a safe criterion for determining the dissociating power of a solvent, although comparisons of this kind are frequently made in support of the rule. For example, in the case of the molecular conductivities of silver nitrate in pyridine and butyronitrile, if it be assumed that the speed of the ions in pyridine is materially greater than in butyronitrile, then the molecular conductivity in pyridine may be greater than in butyronitrile, even though the number of dissociated molecules be somewhat less, as is required if we assume the Nernst-Thomson rule to hold. In the cases cited in Tables VIII and IX the degree of dissociation could not be computed from the electrical conductivity measurements, as no maximum value for the molecular conductivity was obtained. And since, in the case of pyridine and benzonitrile solutions, Werner<sup>1</sup> found normal molecular weights for silver nitrate by boiling-point determinations, this means of calculating the degree of dissociation could of course not be applied.<sup>2</sup> Hence on the basis of the experimental evidence which can be applied in these cases, they must be considered exceptions to the Nernst-Thomson rule.

In this connection it may be well to note a few other exceptions to the Nernst-Thomson rule. The cryoscopic and electrical conductivity measurements by Zanninovich-Tessarini<sup>3</sup> show that potassium chloride dissolved in formic acid is highly dissociated, as one would expect from the high dielectric constant

<sup>1</sup> *Zeit. anorg. Chem.* 15, 1, (1897).

<sup>2</sup> Compare Kahlenberg, *Jour. Phys. Chem.* 3, pp. 397-399 on this point.

<sup>3</sup> *Zeit. phys. Chem.* 19, 251, (1896).

[D. C. = 62] of the latter. But solutions of hydrochloric acid in this solvent show but slight dissociation. Nernst<sup>1</sup> in referring to this case assumes that some specific influence of the solvent comes into play, probably the association of the ions with the molecules of the solvent.

Another exception is noted by Franklin and Kraus<sup>2</sup> in their researches on the electrical conductivity of liquid ammonia solutions. Mercuric cyanide, according to Ostwald,<sup>3</sup> is not at all dissociated in water, but Franklin and Kraus find that in ammonia it forms a solution which possesses a distinct conductivity. Again, the phenols yield good conducting solutions in ammonia, while in water they form solutions which have relatively low conductivity. The following table illustrates this point. It gives the molecular conductivities of orthonitro-phenol in water at 18° C. and in liquid ammonia at -38° C.

TABLE X.

WATER <sup>4)</sup>		LIQUID AMMONIA <sup>5)</sup>	
V.	U.	V.	U.
250	4.09	366.2	82.76
500	5.14	2299.0	148.3
1000	7.24	10380.0	203.9
2000	10.30	63880.0	240.1
U $\infty$ = 355			

Choral and ethyl acetate, according to Drude,<sup>6</sup> have the values 6.67 and 5.85, respectively, for their dielectric constants. The former, according to Kahlenberg and Lincoln,<sup>7</sup> yields solutions with ferric chloride which show no appreciable conduction, while the latter yields solutions with it, which show a distinct conductivity. From the work of the same investigators we see

<sup>1</sup> "Theoretische Chemie," p. 365. (Dritte Auflage).

<sup>2</sup> Am. Chem. Journal, 23, 207, (1900).

<sup>3</sup> Grundlinien der anorg. Chem. p. 667.

<sup>4</sup> Bader: Zeit. phys. Chem. 6, p. 286, (1880).

<sup>5</sup> Am. Chem. Jour. 23, p. 295, (1900).

<sup>6</sup> Zeit. phys. Chem. 23, p. 309, (1897).

<sup>7</sup> Jour. Phys. Chem. 3, 12, (1899).

that ferric chloride does not yield conducting solutions with ethylene chloride [D. C. = 11.3<sup>1</sup>], but it yields solutions with several other solvents having dielectric constants of about the same order or even less, which have very distinct conductivity. Here, then, we have a number of additional exceptions to the Nernst-Thomson rule.

The exceptions to the Nernst-Thomson rule noted above in connection with liquid ammonia solutions, however, do not indicate the general behavior of ammonia solutions of the common salts. While it is true that ammonia solutions for the most part show greater molecular conductivity than aqueous solutions of the same concentration, yet the degree of dissociation is as a rule less than that of the corresponding aqueous solutions. This point is well illustrated by the following table taken from the work of Franklin and Kraus.<sup>2</sup> It shows the dilution at which dissociation reaches 90% in the two solvents.

TABLE XI.

Solute.	Water at 18°C.	Ammonia at -33°.
KI .....	20.0	2000
K Br.....	20.0	4000
K NO <sub>3</sub> .....	25.0	5000
Na Br.....	32.0	2500
Na NO <sub>3</sub> .....	33.0	4000
NH <sub>4</sub> Cl.....	25.0	5000
Ag NO <sub>3</sub> .....	40.0	1500

Carrara's scheme for comparing the dissociating power by calculating the dilution for the same solute in which a definite degree of dissociation is obtained by electrical conductivity measurements; seems an excellent one to apply in this connection to solvents which yield good conducting solutions. In the following table the volumes of the solvents enumerated correspond to

<sup>1</sup> Jahn and Möller: Zeit. phys. Chem. 13, 335, (1894).

<sup>2</sup> Am. Chem. Jour. 23, 297, (1900).

a degree of dissociation equal to 76%, according to Carrara,<sup>1</sup> the solute being tri-ethylsulphine iodide,  $(C_2H_5)_3 SI$ . Under V the volume in liters is given in which one gram molecule of substance is dissolved. The dielectric constants in the second column are those found by Drude, while those in the third column are taken from the results of Nernst, Tereschin, and Thwing. According to the Nernst-Thomson rule the volumes should increase as the D. C. decreases.

TABLE XII.

Solvent.	D. C.	D. C.	Volume.
Water .....	81.0	80	8
Methyl alcohol.....	32.5	32.6	39.6
Ethyl alcohol.....	21.7	25.8	504.0
Propyl alcohol .....	12.3	22.8	1015.0
Allyl alcohol.....	20.6	21.6	89.0
Acetone.....	20.7	21.8	498.0

An inspection of the table shows that with one exception there is a general parallelism between dissociating power and dielectric constant, but the example of allyl alcohol is certainly a striking exception.

Table XIII gives the approximate volumes of various solvents in liters in which a gram molecule of potassium iodide is dissociated to the extent of 75%.

TABLE XIII.

Solvent.	D. C.	Volume.
Water.....	80.	0.4
Methyl alcohol.....	32.5	29
Liquid ammonia.....	22.0	400
Acetone.....	20.5	128
Pyridine.....	12.4	1100

In this case we have another exception in liquid ammonia and acetone.

<sup>1</sup> Zeit. Elektrochem. 4, 475, (1897-98).

When the exceptions noted are considered collectively it becomes evident that the Nernst-Thomson rule must relinquish a good share of the prestige it has hitherto enjoyed. While it is true that in these pages a number of new examples supporting the rule have been given, yet the exceptions noted are of a kind not to be underrated. The rule as it now stands is no more general than the hypothesis of Brühl which attempts to account for the dissociating power of solvents by assuming spare valences to exist, or the parallelism that Dutoit and Aston claim between dissociating power and polymerization of the molecules of the solvent. These theories have been shown to be inadequate by Lincoln,<sup>1</sup> Euler,<sup>2</sup> and Kahlenberg.<sup>3</sup> These investigators cite striking exceptions to these theories and therefore hold them untenable. Hence until we have some experimental evidence in place of the speculative "specific influences" which are said to exist and to account for exceptions to the Nernst-Thomson rule, it must be considered inadequate in accounting for the dissociating power of solvents by virtue of their high specific inductive capacity.

*Relation between the dielectric constant and the latent heat of evaporation.*—Since Louguinine<sup>4</sup> and Kahlenberg<sup>5</sup> have recently determined the latent heat of evaporation of a number of nitriles it seemed of interest to see how closely Obach's law, that the ratio between the dielectric constant and the latent heat of evaporation is approximately a constant for an homologous series, holds for the nitriles. The following table gives the latent heats of evaporation, the dielectric constants, and in the column headed  $\frac{L}{D \cdot C}$  the ratio of the heat of evaporation to the dielectric constant:

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<sup>1</sup> Jour. Phys. Chem. 3, 457, (1899).

<sup>2</sup> Zeit. phys. Chem. 28, 619, (1899).

<sup>3</sup> Jour. Phys. Chem. June (1901).

<sup>4</sup> Compt. Rend., 132, 88, (1901).

<sup>5</sup> Jour. Phys. Chem. 5, 215, (1901)

TABLE XIV.

Substance.	L. H.	D. C.	L. H. / D. C.
Acetonitrile .....	173.6	38.4	4.77
Propionitrile .....	134.4	23.5	5.07
Butyronitrile .....	115.25	20.3	5.48
Valeronitrile .....	95.96	17.4	5.51
Capronitrile .....	83.09	15.5	5.68

The ratios can hardly be said to be constant although the values obtained for the nitriles show as close an agreement as the values Obach had in hand when he indicated the relation between dielectric constant and heat of vaporization, as will appear from the following table which has been selected for comparison:<sup>1</sup>

TABLE XV.

Substance.	L. H.	D. C.	Ratio.
Methyl formate .....	105.8	9.9	10.7
Ethyl formate .....	91.9	9.1	10.1
Propyl formate .....	83.7	9.0	9.3
Iso-butyl formate .....	75.7	8.4	9.0
Amyl formate (iso) .....	71.0	7.7	9.2

#### Conclusion.

The principal points in the foregoing presentation may be summarized in the following general statements:

1. The values of the dielectric constants for the homologous series of compounds examined decrease with increase of molecular weight.

2. The introduction of the cyanogen group in a compound causes a marked increase in the value of the dielectric constant. In this respect the cyanogen radical produces a greater effect than all other radicals which have hitherto been systematically studied.

<sup>1</sup> Phil. Mag. 32, p. 117, (1891).



3. The cyanogen (CN), amido (NH)<sub>2</sub>, or nitric acid (NO<sub>3</sub>) radicals when present in compounds do not cause anomalous absorption as Drude found for the hydroxyl (OH) group.

4. A number of new examples have been given which follow the Nernst-Thomson rule.

5. Some striking exceptions to the Nernst-Thomson rule have been pointed out from which it has been argued that the rule is inadequate. The exceptions indicate that the nature of the solvent as well as the dissolved substance are of prime importance in determining whether a solution will conduct electricity.

6. Obach's law holds only approximately for the nitriles.

This investigation was made in the Laboratory of Physical Chemistry of the University of Wisconsin. It was undertaken at the suggestion of Professor Kahlenberg and carried on under his supervision. As before stated, I am indebted to him for placing at my disposal many of the solvents used for these measurements, and I am under many obligations to him for his helpful suggestions and for the active interest he has always shown in my work; and I am glad to have this opportunity of acknowledging it.

A portion of the results of the work on the nitriles has previously been published in a preliminary article in the *Journal of Physical Chemistry* 5, 157, (1901). For the sake of completeness the results have also been incorporated in the present paper.

*Laboratory of Physical Chemistry,  
University of Wisconsin,  
Madison, May, 1901.*